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<p>(51) International Patent Classification⁷: C 08 G 65/44</p> <p>(21) International Patent Application Number PCT/JP03/02302</p> <p>(22) Date of International Patent Application 28th February 2003 (28.02.2003)</p> <p>(25) Language of international application Japanese</p> <p>(26) Language in which made internationally public Japanese</p> <p>(30) Preferential Claims Data Tokugan 2002 / 63626 8th March 2002 (08.03.2002) JP</p> <p>(71) Patent Applicant (With reference to all the countries indicated in the list excluding the United States of America)</p>	<p>ASAHI KASEI KAISHA) (ASAHI CHEMICALS CO. LTD.) [JP / JP] PIN 530 – 8205, Oosaka fu, Oosaka shi, Kita ku, Daijima Hama, 1 cho me, 2 ban, 6 go. Oosaka (JP).</p> <p>(72) Inventor ; as well as (75) Inventors / (Patent Applicants) (Only with reference to the United States of America) MITSUI, Akira [JP / JP]; Pin 299 - 0261 Chiba ken, Sadegaura Fukutama Dai, 3 - 16 - 2 Chiba (JP). FURUKAWA, Hiroaki [JP/JP]; PIN 299 – 0264, Chiba ken, Sadegaura shi, Imai 3 – 13 - 1, Chiba (JP). OTA, Nobuyuki [JP / JP]; Pin 299 – 0264, Chiba ken, Sadegaura shi, Fukutama Dai 3 – 10 – 1, Asahi Kasei Taku 2 – 13 Chiba</p> <p>(81) Indicated Countries (Domestic): CN, KR, SG, US.</p> <p>Appended documents: - Internal Search Report Regarding 2 character code as well as abbreviation other than those, refer to the” Guidance Note of the code and abbreviations” that has been published in the beginning of the Gazette of the PCT that is regularly published.</p> <p>(54) Title : LOW MOLECULAR WEIGHT POLYPHENYLENE ETHER</p>
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(57) Abstract:

Low molecular weight polyphenylene ether having reduced viscosity measured at 30°C over the chloroform solution of 0.5 g/dl o 0.04 ~ 0.18 dl/g and molecular weight distribution of 1.5 ~ 2.5, or low molecular weight polyphenylene ether powder containing the same, possesses high heat resistance and electrical properties and it is useful as electronic material of print substrate etc. or as improving agent of other resins.

A Detailed Description**Low Molecular Weight Polyphenylene Ether.****<Technical Field>**

The present invention relates to low molecular weight polyphenylene ether. In further details, the present invention relates to low molecular weight polyphenylene ether having excellent heat resistance, electrical properties and solubility in different solvent or reagents and excellent mixing property and reactivity with other components. Furthermore, the present invention also relates to method for manufacture of this low molecular weight polyphenylene ether, and low molecular weight polyphenylene ether obtained by this method.

<Technical Background>

Product or part having desired shape can be produced from polyphenylene ether by fusion injection molding method or fusion extrusion molding method due to its excellent operability and productivity due to which it is being widely used as material of products and parts in different fields such as electrical, electronic, automobile and other industrial fields such as food and packing industry.

Many methods have been proposed as manufacturing method of polyphenylene ether such as those presented in Patent number Sho 36 – 18692, American Patent 3306875, American Patent 3344116, American Patent 3432466 etc.

Polyphenylene ether obtained by these methods used in the applications mentioned above is a high molecular weight polymer having reduced viscosity of more than 0.3 dl/g. However, polyphenylene ether having extremely low molecular weight is being anticipated to be effective in electronic application such as print substrate etc. as compared to high molecular weight polyphenylene ether. Recently,

wiring of the conductor gets damaged with high integration of electronic materials such as print substrate etc. and it is given out as damaged part or heat. Therefore, high heat resistance and low dielectric constant is required in the print substrate material. Moreover, in the process of manufacturing print substrate, material is dissolved in solvent and functionalizing is carried out by denaturation reaction after which it is hardened (cured). Therefore, it is also required to have excellent solubility in solvent and reactivity with other components.

Low molecular weight polyphenylene ether has been presented in Patent number Sho 50 – 6520, Sho 62 – 39628, American patent 6211327 etc., however, low molecular weight polyphenylene ether obtained by any of these methods does not have sufficient heat resistance and electrical properties.

The method to manufacture polyphenylene ether in the mixed solvent of aromatic hydrocarbon such as benzene, toluene, xylene etc. and aliphatic hydrocarbon such as n – hexane, iso hexane, n – heptane etc. has been presented in Patent number Sho 50 – 6520. However, the obtained low molecular weight polyphenylene ether cannot be said to have sufficient heat resistance and electrical properties and furthermore, as becomes clear in practical examples, reduced viscosity is less than 0.2 dl/g and moreover, low molecular weight polyphenylene ether obtained in the low molecular weight region adheres to the reactor etc. resulting in lowering the yield.

In the case of using good solvent of polyphenylene ether (in the above patents, aromatic hydrocarbon such as benzene, toluene, xylene etc.) as the polymerization solvent of polyphenylene ether, the good solvent mentioned above is miscible with the obtained polyphenylene ether due to which at low molecular weight, it adheres to the reactor due to which not only yield lowers, but large equipments are required for removing the good solvent from the polyphenylene ether and controlling of temperature of the equipment becomes complicated. Therefore, reduced viscosity of the obtained low molecular weight polyphenylene ether stops at 0.2 dl/g.

The method to manufacture low molecular weight polyphenylene ether having number-average molecular weight of less than 2800 by using uni-functional alcohol having 1 ~ 5 carbon atoms as polymerization solvent, and water as per requirement has been presented in Patent number Sho 62 – 39628. However, it has many problems such as the obtained low molecular weight polyphenylene ether does not have sufficient heat resistance and electrical properties, yield is only 95 % (actually, in practical examples, it is less than 90 %) and, polymerization takes long time as described in practical examples and therefore, this method cannot be called as industrially useful method.

The method to manufacture low molecular weight polyphenylene ether by removing the catalyst component in the aqueous phase from the polymerization solution of low molecular weight polyphenylene ether and then, directly degassing the good solvent of polyphenylene ether from the polyphenylene ether (for example, using degassing extruder etc.) has been presented in American Patent 6211327. This method relates to manufacture of extremely low molecular weight polyphenylene ether having reduced viscosity of approximately 0.1 dl/g or less than that and this method does not have the problem of yield. However, heat resistance and electrical properties are not sufficient.

Furthermore, low molecular weight polyphenylene ether obtained by these methods is in the granular particles form or pellet form. Its dissolution in solvent takes long time as it possesses large particles and therefore, does not dissolve completely and adheres to the walls of reactor etc.

<Display of invention>

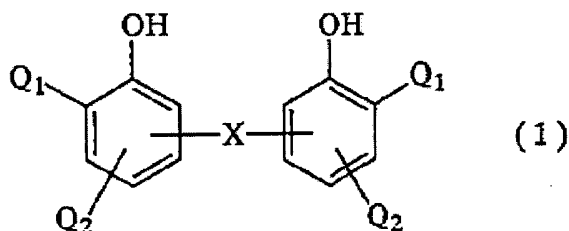
The present invention aims at offering low molecular weight polyphenylene ether having excellent heat resistance, electrical properties and solubility in solvents etc. Furthermore, the present invention also aims at offering a method to manufacture this low molecular weight polyphenylene ether.

The authors of the present invention carried out an earnest research in order to solve the problems mentioned above and the present invention was completed.

Namely, the present invention relates to

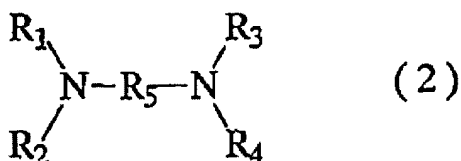
1. The low molecular weight polyphenylene ether that has the characteristic of having reduced viscosity measured at 30°C over chloroform solution having concentration of 0.5 g/dl, of 0.04 ~ 0.18 dl/g and molecular weight distribution of 1.5 ~ 2.5,
2. The low molecular weight polyphenylene ether described above in (1) in which glass transition temperature (T_g) is shown by the following formula,
$$T_g (^{\circ}\text{C}) > 600 \times [\eta_{\text{sp}} / c] + 105$$
3. The polyphenylene ether powder that is formed from low molecular weight polyphenylene ether described above in (1) or (2),
4. The polyphenylene ether powder described above in (3) that has average particle diameter of 5.0 ~ 1000 μm,
5. The polyphenylene ether powder described above in (3) that has average particle diameter of 5.0 ~ 500 μm,
6. The polyphenylene ether powder described above in (3) that has average particle diameter of 5.0 ~ 300 μm,

7. The polyphenylene ether powder described above in (3) that has average particle diameter of 5.0 ~ 100 μm ,
8. The polyphenylene ether powder described above in (3) that essentially does not contain particles of more than 1000 μm ,
9. The low molecular weight polyphenylene ether described above in (1) that is obtained by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas,
10. The low molecular weight polyphenylene ether described above in (9) in which phenol compound is 2, 6 – di methyl phenol,
11. The low molecular weight polyphenylene ether described above in (9) in which phenol compound is mixture of 2, 6 – di methyl phenol and 2, 3, 6 – tri methyl phenol,
12. The low molecular weight polyphenylene ether described above in (9) in which phenol compound is mixture of 2, 6 – di methyl phenol and 2, 6 – di phenyl phenol,
13. The low molecular weight polyphenylene ether described above in (10) ~ (12) in which phenol compound contains divalent phenol shown by the formula (1),



(Wherein, Q1 and Q2 show substitution radical that is hydrogen, alkyl radical, substituted alkyl radical, alalkyl radical, substituted alalkyl radical, aryl radical, substituted aryl radical, alkoxy radical, substituted alkoxy radical or halogen, which can be identical or different: X shows aliphatic hydrocarbon residual radical and their substituted derivatives, oxygen, sulfur or sulfonyl radical and bond position of Q2 and X is ortho or para with respect to phenol hydroxyl radical.)

14. The low molecular weight polyphenylene ether described above in (9) in which catalyst is formed from copper compound, halogen compound and di amine compound shown by the formula (2),



(Wherein, R1, R2, R3 and R4 independently show hydrogen or straight chain or branched alkyl radical having 1 ~ 6 carbon atoms and all these cannot be hydrogen at the same time. R5 shows alkylene radical having 2 ~ 5 carbon atoms having straight chain or methyl branch)

15. The low molecular weight polyphenylene ether described above in (14) in which the catalyst further contains at least tertiary mono amine compound and secondary mono amine compound,
16. The method for manufacture of low molecular weight polyphenylene ether described above in (1) has the following characteristics. Namely, in the method to manufacture low molecular weight polyphenylene ether by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas using good solvent of low molecular weight polyphenylene ether and depositing low molecular weight polyphenylene ether by adding poor solvent to the polyphenylene ether solution obtained by polymerization, the deposition mentioned above is carried out at $-80^{\circ}\text{C} \sim 20^{\circ}\text{C}$,
17. The method described above in (16) in which the poor solvent is alcohol having 1 ~ 10 carbon atoms,
18. The method described above in (16) in which the poor solvent is chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol,
19. The method described above in (18) in which the poor solvent further contains water,
20. The method for manufacture of low molecular weight polyphenylene ether described above in (1) has the following characteristics. Namely, in the method to manufacture low molecular weight polyphenylene ether by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas using good solvent of low molecular weight polyphenylene ether and depositing low molecular weight polyphenylene ether by adding poor solvent to the polyphenylene ether solution obtained by polymerization, polymerization solvent is mixed solvent of 2 or more alcohols,
21. The method described above in (20) in which the mixed solvent is the mixed

- solvent of 2 or more alcohols having 1 ~ 10 carbon atoms,
22. The method described above in (16) in which the polymerization solvent is mixed solvent of 2 or more alcohols chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol,
 23. The method described above in (16) or (20) that includes the process of refining the deposited slurry containing low molecular weight polyphenylene ether by washing and the washing solvent is chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol,
 24. The method described above in (23) in which the washing solvent further contains water,
 25. The method described above in (23) in which the solvent is removed by drying or directly degassing the low molecular weight polyphenylene ether after washing, and
 26. The method described above in (16) or (20) in which wet low molecular weight polyphenylene ether is obtained by separating it from the deposited slurry containing low molecular weight polyphenylene ether and the solvent is removed by drying or directly degassing it.

<Most desired state for practicalization of the invention>

Low molecular weight polyphenylene ether of the present invention has reduced viscosity measured at 30⁰C over chloroform solution having concentration of 0.5 g/dl, of 0.04 ~ 0.18 dl/g and molecular weight distribution (Mw / Mn) of 1.5 ~ 2.5.

Reduced viscosity can be measured at 30⁰C by forming the chloroform solution of polyphenylene ether with concentration of 0.5 g/dl using Ubelhode viscometer. Reduced viscosity of the low molecular weight polyphenylene ether of the present invention should be within the range from 0.04 ~ 0.18 dl/g, desirably 0.04 ~ 0.15 dl/g and further desirably 0.05 ~ 0.13 dl/g.

Molecular weight distribution can be measured by using gel permeation chromatography (GPC). Standard polystyrene is desired to be used for detecting molecular weight. Moreover, GPC – LALL that combines GPC and light scattering method can also be used. Molecular weight distribution (Mw / Mn) of the low molecular weight polyphenylene ether of the present invention should be within the range from 1.5 ~ 2.5, desirably 1.6 ~ 2.4. Low molecular weight polyphenylene ether having molecular weight distribution within this range has excellent heat resistance and electrical properties as compared to low molecular weight polyphenylene ether having molecular weight distribution outside this range even if it possesses same

reduced viscosity.

Low molecular weight polyphenylene ether of the present invention possesses excellent heat resistance. Glass transition temperature (T_g) is used as the index of heat resistance of polyphenylene ether. Low molecular weight polyphenylene ether of the present invention is desired to have glass transition temperature shown by the following formula.

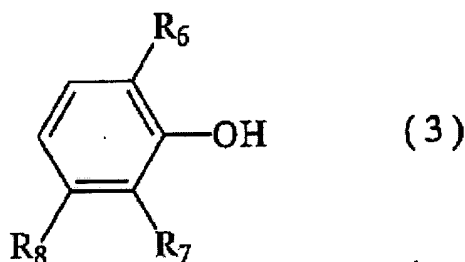
$$T_g (^{\circ}\text{C}) > 600 \times [\eta_{\text{sp}} / c] + 105$$

Wherein, T_g shows glass transition temperature of low molecular weight polyphenylene ether expressed in centigrade and $[\eta_{\text{sp}} / c]$ shows reduced viscosity (unit: dl/g) of the low molecular weight polyphenylene ether measured at 30°C over the chloroform solution having concentration of 0.5 g/dl.

The low molecular weight polyphenylene ether of the present invention is desired to be in powder state from the viewpoint of solubility in solvents. Average particle diameter of the low molecular weight polyphenylene ether powder of the present invention should be within the range from 5.0 ~ 1000 μm , desirably 5.0 ~ 500 μm , more desirably, 0.5 ~ 300 μm and most desirably 5.0 ~ 100 μm , and it is desired not to essentially contain particles of more than 1000 μm .

The low molecular weight polyphenylene ether of the present invention can be obtained by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas.

The phenol compound used in the present invention possesses the structure shown by the general formula (3) given below.

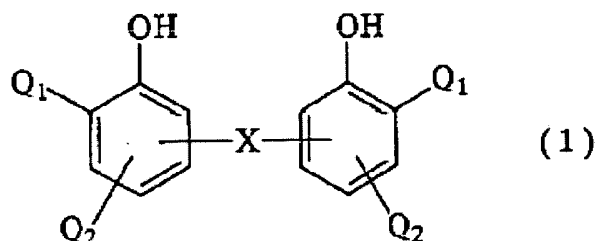


Wherein, R_6 , R_7 and R_8 independently show substitution radical, R_6 shows alkyl radical, substituted alkyl radical, alalkyl radical, substituted alalkyl radical, aryl radical, substituted aryl radical, alkoxy radical, substituted alkoxy radical, R_7 and R_8 show same radicals as that of R_6 plus hydroxide and halogen.

As regards the examples of compound mentioned above, o - cresol, 2, 6 - di methyl phenol, 2, 3, 6 - tri methyl phenol, 2 - ethyl phenol, 2 - methyl - 6 - ethyl phenol, 2, 6 - di ethyl phenol, 2 - n - propyl phenol, 2 - ethyl - 6 - n - propyl phenol, 2 - methyl - 6 - chloro phenol, 2 - methyl - 6 - bromo phenol, 2 - methyl - 6 - iso

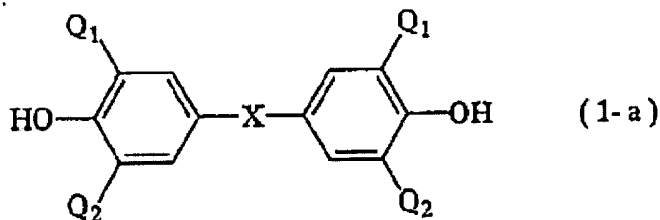
propyl phenol, 2-methyl-6-n-propyl phenol, 2-ethyl-6-bromo phenol, 2-methyl-6-n-butyl phenol, 2,6-di propyl phenol, 2-ethyl-6-chloro phenol, 2-methyl-6-phenyl phenol, 2-phenyl phenol, 2,6-di phenyl phenol, 2,6-bis-(4-fluoro phenyl) phenol, 2-methyl-6-toluy phenol, 2,6-di toluy phenol etc. can be given. These compounds can be used independently or as a mixture. Moreover, these can contain small quantity of m-cresol, p-cresol, 2,4-di methyl phenol, 2,4,6-tri methyl phenol. Among these also, 2,6-di methyl phenol is industrially important. Moreover, combination of 2,6-di methyl phenol and 2,3,6-tri methyl phenol, or combination of 2,6-di methyl phenol and 2,6-di phenyl phenol is desired to be used.

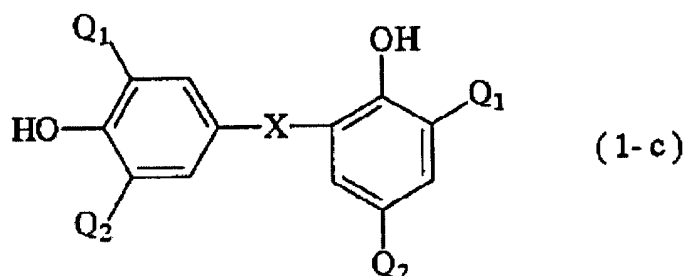
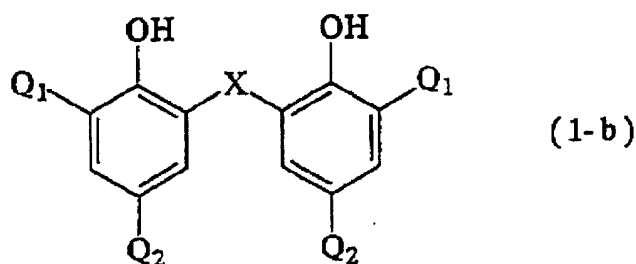
Moreover, phenol compound is desired to contain divalent phenol shown by the general formula (1) given below.



Wherein, Q1 and Q2 show hydrogen, alkyl radical, substituted alkyl radical, alalkyl radical, substituted alalkyl radical, aryl radical, substituted aryl radical, alkoxy radical, substituted alkoxy radical or halogen, which can be identical or different: X shows aliphatic hydrocarbon residual radical and their substituted derivatives, oxygen, sulfur or sulfonyl radical and bond position of Q2 and X is ortho or para with respect to phenol hydroxyl radical.

As regards the examples of the compound mentioned above, compounds having different structures shown by (1-a), (1-b) and (1-c) can be given.





Wherein, Q1 and Q2 show hydrogen, alkyl radical, substituted alkyl radical, alalkyl radical, substituted alalkyl radical, aryl radical, substituted aryl radical, alkoxy radical, substituted alkoxy radical or halogen, which can be identical or different: X shows aliphatic hydrocarbon residual radical and their substituted derivatives, oxygen, sulfur or sulfonyl radical.

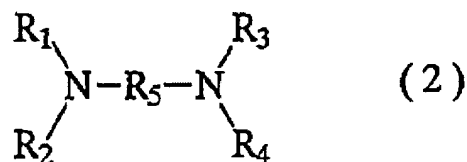
As regards the representative examples of compounds having the structure of general formulae given above, compound in which Q1 and Q2 are methyl radicals and X is iso propylidene, compound in which Q1 and Q2 are methyl radicals and X is methylene, compound in which Q1 and Q2 are methyl radicals and X is thio, compound in which Q1 and Q2 are methyl radicals and X is cyclo hexylidene etc. can be given, however, it is not restricted to these examples.

These divalent phenyl type compounds can be used independently or as a mixture of 2 or more. There is no particular restriction over the content of divalent phenol type compound, however, it should be within the range from 0.1 ~ 30 mol % with respect to monovalent phenol.

All the well-known catalysts commonly used in the manufacture of polyphenylene ether can be used as catalyst used in the present invention. As regards the catalyst, catalyst formed from transition metal ion to having oxidation reduction functionality and amine compound that can form complex with this metal ions is known, for example, catalyst system formed from copper compound and amine, catalyst system formed from manganese compound and amine, catalyst system formed from cobalt compound and amine etc. can be given. Polymerization reaction progresses well under slightly alkaline conditions due to which little quantity of alkali

or amine is added.

Among these also, catalyst formed from copper compound, halogen compound and di amine compound shown by the general formula (2) given below is desired to be used.



Wherein, R₁, R₂, R₃ and R₄ independently show hydrogen or straight chain or branched alkyl radical having 1 ~ 6 carbon atoms and all these cannot be hydrogen at the same time. R₅ shows alkylene radical having 2 ~ 5 carbon atoms having straight chain or methyl branch.

The examples of copper compound that is the catalyst component have been given. As regards the copper compound, cuprous compound, cupric compound or their mixture can be used. As regards the cupric compound, cupric chloride, cupric bromide, cupric sulfate, cupric nitrate etc. can be given. Moreover, as regards the cuprous compound, cuprous chloride, cuprous bromide, cuprous sulfate, cuprous nitrate etc. can be given. Among these also, cuprous chloride, cupric chloride, cuprous bromide and cupric bromide are desired to be used. Moreover, these copper salts can be synthesized from halogen or acid for obtaining oxide, carbonate salt, hydroxide etc. at the time of using. It can be prepared by mixing cuprous oxide with hydrogen halide (or solution of hydrogen halide).

As regards the halogen compound, hydrogen chloride, hydrogen bromide, hydrogen iodide, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide, tetra methyl ammonium chloride, tetra methyl ammonium bromide, tetra methyl ammonium iodide, tetra ethyl ammonium chloride, tetra ethyl ammonium bromide, tetra ethyl ammonium iodide etc. can be given. Moreover, these can be used as aqueous solution or solution formed by using appropriate solvent. These halogen compounds can be used independently or as a mixture of 2 or more. Aqueous solution of hydrogen chloride and aqueous solution of hydrogen bromide are desired to be used as halogen compound.

There is no particular restriction over the quantity with which these compounds are used, however, copper atoms should be within the range from 0.02 ~ 0.6 mol with respect to 100 moles of phenol compound and halogen atoms should be within the range from 2 ~ 20 times with respect to molar weight of copper atoms.

Next, examples of di amine compound that is the catalyst component have been

given below. Namely, N, N, N', N' – tetra methyl ethylene di amine, N, N, N' – tri methyl ethylene di amine, N, N' – di methyl ethylene di amine, N, N, - di methyl ethylene di amine, N – methyl ethylene di amine, N, N, N', N' – tetra ethyl ethylene di amine, N, N, N' – tri ethyl ethylene di amine, N, N' – di ethyl ethylene di amine, N, N, - di ethyl ethylene di amine, N – ethyl ethylene di amine, N, N – di methyl – N' – ethyl ethylene di amine, N, N' – di methyl – N – ethyl ethylene di amine, N – n – propyl ethylene di amine, N, N' – n – propyl ethylene di amine, N – i – propyl ethylene di amine, N, N' – i – propyl ethylene di amine, N – n – butyl ethylene di amine, N, N' – n – butyl ethylene di amine, N – i – butyl ethylene di amine, N, N' – i – butyl ethylene di amine, N – t – butyl ethylene di amine, N, N' – t – butyl ethylene di amine, N, N, N', N' – tetra methyl – 1, 3 – di amino propane, N, N, N' – tri methyl – 1, 3 – di amino propane, N, N' – di methyl – 1, 3 – di amino propane, N – methyl – 1, 3 – di amino propane, N, N, N', N' – tetra methyl – 1, 3 – di amino – 1 – methyl propane, N, N, N', N' – tetra methyl – 1, 3 – di amino – 2 – methyl propane, N, N, N', N' – tetra methyl – 1, 4 – di amino butane, N, N, N', N' – tetra methyl – 1, 5 – di amino pentane etc. can be given. Desirably, di amine compound in which number of carbon atoms of alkylene radical bonded to 2 nitrogen atoms are 2 or 3 is used. There is no particular restriction over the quantity with which this di amine compound is used, however, it should be used with the quantity of 0.01 ~ 10 mol with respect to 100 moles of phenol compound.

As regards the composition component of catalyst of the present invention, tertiary monoamine compound or secondary monoamine compound are desired to be used independently or as a mixture.

Tertiary monoamine compound is aliphatic tertiary amine containing cyclic tertiary amine. For example, tri methylamine, tri ethylamine, tri butylamine, tri iso butylamine, di methyl ethylamine, di methyl propylamine, allyl di ethylamine, di methyl – n – butylamine, di ethyl iso propylamine, N – methyl cyclo hexylamine etc. can be given. These tertiary monoamine compound can be used independently or as a combination of 2 or more compounds. There is no particular restriction over the quantity with which these are used, however, these should be used with the quantity of 0.1 ~ 10 mol with respect to 100 moles of phenol compound.

As regards the examples of secondary monoamine compound, secondary aliphatic amines such as di methylamine, di ethylamine, di – n – propylamine, di – iso – propylamine, di – n – butylamine, di – iso – butylamine, di – tert – butylamine, di pentyl amines, di hexyl amines, di octyl amines, di decyl amines, di benzyl amines, methyl ethylamine, methyl propylamine, methyl butylamine, cyclo hexylamine etc.

can be given. As regards the secondary monoamine compounds containing aromatic ring, N – phenyl methanol amine, N – phenyl ethanol amine, N – phenyl propanol amine, N – (m – methyl phenyl) ethanol amine, N – (p – methyl phenyl) ethanol amine, N – (2', 6' – di methyl phenyl) ethanol amine, N – (p – chloro phenyl) ethanol amine, N – ethyl aniline, N – butyl aniline, N – methyl – 2 – methyl aniline, N – methyl – 2, 6 – di methyl aniline, di phenyl amine etc. can be given, however, there is no particular restriction over the same. These secondary monoamine compounds can be used independently or as a combination of 2 or more compounds. There is no particular restriction over the quantity with which these are used, however, these should be used with the quantity of 0.1 ~ 10 mol with respect to 100 moles of phenol compound.

Secondary monoamine compound and tertiary monoamine compound can be independently or in combination as composition component of catalyst.

Furthermore, well-known surfactants having effect of improving polymerization activity are desired to be added. For example, tri octyl methyl ammonium chloride known with the product name Aliquat 336 or Capriquat can be given. The usage quantity should not exceed 0.1 wt % with respect to total quantity of polymerization reaction mixture.

As regards the oxygen-containing gas used in the polymerization of the present invention, oxygen and mixture of oxygen and inert gas such as nitrogen with desired proportion, air and mixture of air and mixture of oxygen and inert gas such as nitrogen with desired proportion can be used. Pressure inside the system in the polymerization reaction should be normal pressure, however, reduced pressure or elevated pressure can be used as per requirement.

There is no particular restriction over the temperature of polymerization, however, if it is too low, then reaction does not progress whereas if it is too high, then selectivity of reaction lowers and therefore, it should be within the range from 0 ~ 80°C, desirably 10 ~ 70°C.

There is no particular restriction over the method of post-treatment performed after the completion of polymerization reaction. Common method of deactivating catalyst by adding acid such as hydrochloric acid or acetic acid, or ethylene di amine tetra acetate (EDTA) or its salt, or nitro tri acetate and its salt etc. can be used.

Moreover, method of treating the by-products such as di phenoquinone that are known to get generated in the polymerization of polyphenylene ether can be used. If metal ions that are catalyst are essentially deactivated, then de-coloration is carried out just by heating. Moreover, method of adding required quantity of reducing agent such as hydroquinone, sodium di thioate (?), can be used. There is no particular

restriction over the temperature of this process, however, it should be within the range from 10 ~ 100°C.

As regards the method to obtain polyphenylene ether, the precipitation method of using poor solvent of polyphenylene ether as polymerization solvent and depositing polyphenylene ether as particles with the progress of the polymerization, and solution polymerization method of using good solvent as polymerization solvent and dissolving polyphenylene ether in the solvent, are known. However, low molecular weight polyphenylene ether of the present invention can be obtained by using either of these methods.

In the case of using the precipitation method of using poor solvent of polyphenylene ether as polymerization solvent and depositing polyphenylene ether as particles with the progress of the polymerization, as regards the poor solvent, mixed solvent of 2 or more alcohols is required to be used.

As regards the poor solvent, alcohol having 1 ~ 10 carbon atoms is desired. For example, 2 or more alcohols chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol are used. This poor solvent should not contain water.

There is no particular restriction over type as long as 2 or more types are used. Moreover, there is no particular restriction over the ratio of each solvent in the mixed solvent and combination and ratio of polymerization solvent required for the method of the present invention can be selected among these solvents.

It was shown that if mixed solvent of 2 or more alcohols is used, then molecular weight of the low molecular weight polyphenylene ether can be controlled by changing their ratio irrespective of it being poor solvent of low molecular weight polyphenylene ether, and that these show peculiar behavior of improving polymerization activity and yield as compared to the case of independently using 1 alcohol.

Good solvent can coexist in the polymerization solvent as long as it does not dissolve the low molecular weight polyphenylene ether. For example, in the case of low molecular weight polyphenylene ether having reduced viscosity of 0.07 dl/g, mixed solvent of methanol and n-butanol can contain small quantity of xylene (1%). If reduced viscosity of polyphenylene ether lowers, then quantity of good solvent is reduced. In the case of low molecular weight polyphenylene ether having reduced viscosity of 0.04 dl/g, permitted quantity of xylene is 50 ppm. Quantity of good solvent differs with the desired reduced viscosity of the low molecular weight polyphenylene ether and degree of miscibility of good solvent with low molecular

weight polyphenylene ether and therefore, it differs with the type of solvent.

On the other hand, in the case of using solution polymerization method of using good solvent as polymerization solvent and depositing low molecular weight polyphenylene ether by adding poor solvent to the obtained solution containing low molecular weight polyphenylene ether, the deposition is required to be carried out at $-80^{\circ}\text{C} \sim +20^{\circ}\text{C}$.

As regards the good solvent, aromatic hydrocarbon such as benzene, toluene, xylene (includes different isomers such as o -, m -, p -), ethyl benzene, styrene, halogenated hydrocarbon such as chloroform, methylene chloride, 1, 2 - di chloro ethane, chlorobenzene, di chlorobenzene, nitro compound such as nitro benzene etc. can be given. Toluene is desired to be used as good solvent. Moreover, as regards the solvents classified as good solvent even if being slightly poor solvent, aliphatic hydrocarbons such as pentane, hexane, heptane, cyclo hexane, cyclo heptane etc., esters such as ethyl acetate, ethyl formate etc., ethers such as tetra hydro furan, di ethyl ether etc., di methyl sulfoxide can be given. These good solvents can be used independently or as a mixture of 2 or more. Furthermore, reaction mixture obtained after polymerization can contain poor solvent such as alcohol or water as long as solution state is maintained.

Solution containing low molecular weight polyphenylene ether and solvent is obtained by polymerization. There is no particular restriction over the concentration of low molecular weight polyphenylene ether in the solvent, however, it should be within the range from 25 ~ 70 weight %.

Low molecular weight polyphenylene ether is deposited by adding poor solvent to the obtained solution. As regards the poor solvent, ethers, ketones or alcohols can be given. Desirably, solvent is alcohol having 1 ~ 10 carbon atoms and more desirably, it is chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol. It can contain water.

There is no particular restriction over the device or method in the method of depositing low molecular weight polyphenylene ether. For example, the method of adding solution containing low molecular weight polyphenylene ether and solvent, and poor solvent continuously to the appropriately sized tank equipped with a stirrer, the method of adding poor solvent to the tank in which solution containing low molecular weight polyphenylene ether is put, the method of adding solution containing low molecular weight polyphenylene ether to the tank in which poor solvent is put, the method of adding solution containing low molecular weight polyphenylene ether and solvent, and poor solvent continuously to the tube type static

mixer, etc. can be used.

There is no particular restriction over the temperature of solution containing low molecular weight polyphenylene ether and temperature of poor solvent supplied to the deposition device, however, temperature of deposition operation carried out in the deposition tank should be sufficiently monitored. Deposition is required to be carried out at $-80 \sim +20^{\circ}\text{C}$ in order to obtain low molecular weight polyphenylene ether of the present invention. If temperature exceeds 20°C , then low molecular weight polyphenylene ether adheres the reactor and it cannot be deposited. On the other hand, if it is less than -80°C , low molecular weight polyphenylene ether can be obtained, however, large amount of energy is required to lower the temperature below -80°C which is not required.

Slurry containing low molecular weight polyphenylene ether and solvent is obtained by any of the methods mentioned above. Low molecular weight polyphenylene ether of the present invention can be obtained by removing the solvent from the slurry. As regards the method to remove solvent, the method in which slurry is separated into solid and liquid to obtain wet low molecular weight polyphenylene ether and low molecular weight polyphenylene ether is obtained by drying or directly degassing it, can be given.

There is no particular restriction over the solid – liquid separation, and well-known methods can be used for the same. For example, filtration type centrifugal separator, scraping blades-attached centrifugal separator, vacuum drum type filter, nuche (?) etc. can be used. Moreover, In the case of slurry obtained by using good solvent as polymerization solvent and depositing at low temperature, first filtration temperature is required to be within the temperature range mentioned above as deposition temperature.

The obtained wet low molecular weight polyphenylene ether is desired to be washed with poor solvent of this low molecular weight polyphenylene ether before drying or directly degassing. As regards the washing solvent, methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol can be used. The washing solvent is further desired to contain water.

The obtained wet low molecular weight polyphenylene ether is dried or directly degassed based on which low molecular weight polyphenylene ether can be obtained. There is no particular restriction over drying method, and well-known methods can be used for the same. For example, For example, paddle dryer, vacuum dryer, spray dryer, heating tube dryer etc. Particularly, drying is desired to be carried out under inert gas. In this drying method, low molecular weight polyphenylene ether of the present

invention is obtained as powder. Direct degassing method is the method of removing volatile solvent by heating the obtained wet polyphenylene ether. For example, the method in which wet low molecular weight polyphenylene ether is supplied to the heated degassing extruder and low molecular weight polyphenylene ether of the present invention taken out from die while degassing the volatile component, is cooled and cut and pellet is obtained, the method in which reactor in which wet low molecular weight polyphenylene ether is taken is heated and its pressure is reduced and low molecular weight polyphenylene ether of the present invention is solidified while removing the solvent and then it is forcefully taken out from the reactor, can be given. Method other than this can be used. In the direct degassing method, the obtained polyphenylene ether is in pellet or large lump state. In the present invention, low molecular weight polyphenylene ether can be powdered by using the method of pulverizing the polyphenylene ether present in this state.

Low molecular weight polyphenylene ether of the present invention has excellent heat resistance and electrical properties and therefore, it is extremely useful as the electronic material requiring low dielectric constant and low dielectric damage. Moreover, low molecular weight polyphenylene ether powder of the present invention has small particle diameter due to which its solubility in solvent at the time of using it in the process of preparing prepreg is excellent and moreover, reactivity with different denaturing reaction agents is also excellent due to which it can be used from the viewpoint of improving productivity of electronic material.

Furthermore, low molecular weight polyphenylene ether of the present invention can be used in different thermoplastic resin composites or thermal hardening type resins. Low molecular weight polyphenylene ether of the present invention has the effect of plasticizing different thermoplastic resin composites and therefore, it can be used as plasticizer. Low molecular weight polyphenylene ether of the present invention can be used in the denatured polyphenylene ether resin in which high molecular weight polyphenylene ether is generally used, and it can contribute to improve its flowability.

As regards the thermoplastic resins, composite of polystyrene group resin (rubber reinforced polystyrene or AS, ABS resin), polyamide resin, polyolefin group resins, polyester resin, liquid crystals resin, thermoplastic resin elastomer etc. can be given. As regards the thermal hardening type resin, composite of epoxy group, unsaturated polyester group, polyurethane, bridging allyl, bis maleimide, phenol type resins etc. can be given. However, there is no particular restriction over these examples. Particularly, low molecular weight polyphenylene ether of the present invention

maintains the flame retardation property originally possessed by polyphenylene ether due to which it is useful as additive for imparting heat resistance and flame retardation property to other resins having bad heat resistance and flame retardation property. Particularly, it is extremely useful for improving polystyrene or thermoplastic resin elastomer.

At the time of manufacturing resin composite containing low molecular weight polyphenylene ether of the present invention, different additives such as plasticizer, stabilizing agent, denaturing agent, ultraviolet rays absorption agent, flame retardation agent, colorant, mold releasing agent, fibrous reinforcing agents such as glass fibers, carbon fibers, fillers such as glass beads, calcium carbonate, talc etc. Can be added. As regards the stabilizing agent or denaturing agent, metal oxides, anhydrous carbonic acids, dienophyl compounds such as styrene or stearyl acrylate etc., epoxy radical-containing compounds etc. can be given. These additives can be used independently or in combination.

Any method can be used as the method of mixing each component composing the resin composite containing low molecular weight polyphenylene ether of the present invention, for example, solution blend and degassing method, extruder, heating roll, bombarding mixer, kneader, Henschel mixer etc. can be given.

<Practical examples>

The present invention has been explained below in further details with the help of practical examples. However, the present invention is not restricted only to these practical examples.

Moreover, measurement was carried out by following methods.

(1) Reduced viscosity [η_{sp} / c]

Chloroform solution containing polyphenylene ether obtained in examples with concentration 0.5 g/dl is prepared and reduced viscosity is measured at 30⁰C using Ubelhode viscometer. Unit is dl/g.

(2) Polyphenylene ether yield

Weight of obtained dry polyphenylene ether with respect to weight of the phenol compound. It is expressed in %.

(3) Molecular weight distribution

It was measured preparing working curve by using ethyl benzene and standard polystyrene by Showa Denko make Gel Permeation Chromatography SHODEX – GPC system 21. Polystyrene having molecular weight of 550, 1300, 2960, 9680, 28600, 65900, 172000, 629000, 996000, 1960000, 3900000 were used standard polystyrene. 2 SHODEX make K-802.5 columns were arranged and used as column.

Moreover, solvent was chloroform, flow rate of solvent was 1.0 ml/min and temperature of column was 40°C. UV detector was used as detector part and wavelength was 254 nm at the time of preparing working curve of standard polystyrene and it was 283 nm at the time of measuring molecular weight of polyphenylene ether. Sample was dissolved in chloroform and solution from which undissolved matter was removed by membrane filter was supplied for measurement. Molecular weight distribution (M_w / M_n) that is the ratio of weight-average molecular weight (M_w) and number-average molecular weight (M_n) was determined.

(4) Polyphenylene ether particle diameter

Polyphenylene ether obtained in different examples was sieved using 1000 μm mesh sieve and quantity of the polyphenylene ether remained on the sieve was measured. Next, polyphenylene ether passed through the sieve was dispersed in methanol and its particle diameter was measured by using Laser Particle Size Analyzing Device SALD – 2000 (Shimazu Seisakujo make). If polyphenylene ether remained on the sieve exceeds 20 wt % of total weight of the sieved polyphenylene ether, then particle diameter > 1000 μm was taken.

(5) Glass transition temperature of polyphenylene ether (T_g)

Glass transition temperature (T_g) was measured by carrying out scanning twice within the temperature 50°C ~ 300°C with the rate of temperature rise of 20°C/min under nitrogen atmosphere using Perkin Elmar make DSC (Differential Scanning Colorimeter) product name Pyris1. T_g was determined from the specific heat curve obtained in second scan.

(6) Dielectric constant of polyphenylene ether

Measurement target polyphenylene ether was press molded by Shindo (Kamifuji ?) Kinzoku Kogyo make Press Molding Machine (Test Press SR – 10) by using mold of 150 mm x 150 mm x 2 mm. A part of obtained press plate was used and its dielectric constant was measured at 1 MHz as per JIS – K6911 standard test method. Hewlett Packard make Presion (?) LCR meter (HP – 4284A) was used as measurement device.

Practical example 1

0.2512 g of cupric chloride hydrate, 1.1062 g of 35 % hydrochloric acid, 3.6179 g of di – n – butylamine, 9.5937 g of N, N, N', N' – tetra methyl propane di amine, 211.63 g of methanol, 493.80 g of n – butanol and 180.0 g of 2, 6 – di methyl phenol were taken in 1.5 liter reactor attached with jacket equipped with super jar for introducing oxygen-containing gas, stirring turbine blades and baffle in the bottom part of the reactor, and reflux condenser in bent gas line on the upper part of the

reactor. Composition ratio of solvent was n – butanol : methanol = 70:30. Next, oxygen was started to introduce in the reactor by super jar with the rate of 180 ml/min simultaneously while vigorously stirring and at the same time, hot medium was circulated through the jacket so as to regulate polymerization temperature at 40°C. Polymerization liquid gradually formed a slurry. No adhesion on the reactor was observed during the polymerization. 120 minutes after introduction of oxygen, circulation of oxygen was stopped and 10 % aqueous solution of ethylene di amine tetra acetate 3 potassium salt (Doni (?) Kagaku Kenkyusho make reagent) was added to the obtained polymerization mixture and temperature was increased to 50°C. Next, hydroquinone (Wako Junyaku make reagent) was added with small quantity and temperature was maintained at 50°C till the slurry form polyphenylene ether becomes white. After the completion, it was filtered and residue wet polyphenylene ether was put in the methanol washing solvent containing 50 % water and it was stirred at 60°C. It was then again filtered and methanol containing 50 % water was added to the residue while stirring when wet polyphenylene ether was obtained. It was vacuum dried at 110°C and dry polyphenylene ether was obtained. Average particle diameter was 56 µm and particles of more than 1000 µm were not present. Moreover, $[\eta_{sp}/c]$, yield, molecular weight distribution, Tg and dielectric constant were measured. The results have been presented in table 1 given below.

Practical example 2

Total quantity of solvents was not changed, however, composition ratio was changed to n – butanol : methanol = 30 : 70. Other than this change, procedure similar to practical example 1 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 34 µm and particles of more than 1000 µm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 3

Total quantity of solvents was not changed, however, composition ratio was changed to n – butanol : methanol = 10 : 90. Other than this change, procedure similar to practical example 1 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 39 µm and particles of more than 1000 µm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Comparative example 1

Total quantity of solvents was not changed, however, composition ratio was changed to n – butanol : methanol = 0 : 100. Other than this change, procedure similar to practical example 1 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 15 μm and particles of more than 1000 μm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Comparative example 2

N – butanol saturated with water was used as solvent and polymerization time was changed to 240 minutes. Other than this change, procedure similar to practical example 1 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 39 μm and particles of more than 1000 μm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Comparative example 3

Total quantity of solvents was not changed, however, composition ratio was changed to xylene : n – butanol : methanol = 60:20:20. Other than this change, procedure similar to practical example 1 was carried out. Adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 920 μm and particles of more than 1000 μm were present with the proportion of 46 %. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Comparative example 4

Polymerization time was changed to 55 minutes. Other than this change, procedure similar to comparative example 3 was carried out. Adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 850 μm and particles of more than 1000 μm were present with the proportion of 38 %. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 4

Mixture formed from 126 g of 2, 6 – di methyl phenol and 54 g of 2, 3, 6 – tri methyl phenol was used as phenol compound. Other than this change, procedure similar to practical example 2 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 43 μm and particles of more than 1000 μm were not present.

Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 5

Mixture formed from 126 g of 2, 6 – di methyl phenol and 54 g of 2, 6 – di phenyl phenol was used as phenol compound, 0.1690 g of N, N, N', N' – tetra methyl ethylene di amine was used as di amine of the catalyst, polymerization temperature was changed to 60⁰C and polymerization time was changed to 180 minutes. Other than this change, procedure similar to practical example 2 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 33 µm and particles of more than 1000 µm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 6

Total quantity of solvents was not changed, however, composition ratio was changed to n – butanol : methanol = 10 : 90 and solvent formed from methanol : water = 90:10 was used as washing solvent. Other than this change, procedure similar to practical example 1 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 54 µm and particles of more than 1000 µm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 7

2, 6 – di methyl phenol containing 5 mol % of 2, 2 – bis (3, 5 – di methyl - 4 – hydroxy phenyl) propane was used as phenol compound. Other than this change, procedure similar to practical example 2 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 42 µm and particles of more than 1000 µm were not present. Moreover, measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 8

Total quantity of solvents was not changed, however, composition ratio was changed to n – butanol : methanol : xylene = 85 : 14.25 : 0.75. Other than this change, procedure similar to practical example 1 was carried out. No adhesion on the reactor was observed during the polymerization. Average particle diameter of the obtained polyphenylene ether was 54 µm and particles of more than 1000 µm were not present. Moreover, measurements similar to practical example 1 were carried out. The results

have been presented in table 1 given below.

Comparative example 5

Experiment was carried out as per the method described in practical examples of American Patent 6211327. Namely, copper bromide and di - n - butylamine were used as catalysts and 2, 6 - di methyl phenol was polymerized in toluene solvent at the temperature range of 40⁰C ~ 45⁰C under oxygen supply simultaneously while stirring and after that, oxygen supply was stopped and aqueous solution of nitrilo tri acetate was added under nitrogen seal simultaneously while stirring and copper catalyst was extracted in aqueous phase and temperature was regulated at 55⁰C and this state was maintained for 70 minutes. Next, the obtained mixture was separated into toluene solution phase in which polyphenylene ether was dissolved and aqueous phase in which copper was dissolved by Sharpless (?) make liquid - liquid centrifugal separator. Toluene was removed and the obtained solution of polyphenylene ether was concentrated till the solid part becomes 65 %, and then degassing extraction was carried out by using degassing extruder when pellet form low molecular weight polyphenylene ether was obtained. Average particle diameter of this pellet was more than 1000 µm and particles of more than 1000 µm were present with the proportion of 97 wt %. [η_{sp} / c], yield, molecular weight distribution, T_g and dielectric constant of the pellet were measured. The results have been presented in table 1 given below.

Practical example 9

Polymerization was carried out as per the method described in Sho 59 - 23332. Namely, 50 weight % toluene solution of 2, 6 - di methyl phenol was added to toluene solution of catalyst formed from copper bromide, hydrogen bromide, N, N' - di - t - butyl ethylene di amine, N, N - di methyl - n - butylamine and di - n - butylamine for 35 minutes simultaneously while circulating oxygen and after 74 minutes, oxygen supply was stopped. Aqueous solution of ethylene di amine tetra acetate 3 sodium salt was added to the polymerization mixture and mixture was kept at 70⁰C. The obtained mixture was separated into toluene solution phase in which polyphenylene ether was dissolved and aqueous phase in which copper was dissolved, by Sharpless (?) make liquid - liquid centrifugal separator. The obtained mixture was sent to Sharpless (?) make centrifugal separator and polyphenylene ether solution containing 26 wt % of polyphenylene ether was obtained. This solution was named as (A). Stirring turbine blades and baffle were installed in the internal part and deposition tank attached with external jacket was prepared and polyphenylene ether solution (A) was added to it under the conditions a of table 2. Cooling medium was flown through the jacket simultaneously while stirring and temperature was maintained at - 10⁰C. Methanol

having its temperature maintained at -10°C was added with the quantity as per conditions a of table 2. At this time, weight ratio of poor solvent methanol and good solvent toluene was methanol / toluene = 2.5. Solutions were mixed and dispersed and slurry deposited with polyphenylene ether was obtained after which this mixture was filtered by nuche (?) and it was washed with methanol at -10°C simultaneously while stirring. After that, the obtained residue was vacuum dried at 140°C for 1 hour.

Average particle diameter of the obtained polyphenylene ether was $42\text{ }\mu\text{m}$ and particles of more than $1000\text{ }\mu\text{m}$ were not present. Measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below. Same operation was carried out with the weight ratio of poor solvent methanol and good solvent toluene of methanol / toluene = 5.0 (condition b), 7.0 (condition c) and 12.0 (condition d). In any of the conditions, polymer was deposited as particles and particles of more than $1000\text{ }\mu\text{m}$ were not present. Measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Practical example 10

Similar to practical example 9, constant deposition temperature was taken as 1°C and procedure was carried out as per condition a when polymer was deposited as particles and particles of more than $1000\text{ }\mu\text{m}$ were not present. Measurements similar to practical example 1 were carried out. The results have been presented in table 1 given below.

Comparative example 6

Similar to practical example 9, constant deposition temperature was taken as 30°C and procedure was carried out as per condition a when the deposited polymer was viscous and stirring turbine blade stopped and a lump was formed and further operation could not be carried out.

Table 1. Table of Results

Experiment number	η_{sp} / c [dl/g]	Yield [%]	Average particle diameter μm	Mw/M n	Tg [$^{\circ}\text{C}$]	Dielectri c constant
Practical example 1	0.116	97	56	1.89	185	2.49
Practical example 2	0.082	98	34	1.87	167	2.52
Practical example 3	0.075	98	39	1.92	155	2.55
Comparative example 1	0.070	88	15	1.35	135	2.80
Comparative example 2	0.072	76	39	2.56	142	2.71
Comparative example 3	0.476	97	920	2.58	215	2.45
Comparative	0.195	64	850	2.39	205	2.47

example 4						
Practical example 4	0.081	98	43	1.85	178	2.48
Practical example 5	0.079	97	33	2.10	180	2.50
Practical example 6	0.085	98	54	1.89	169	2.48
Practical example 7	0.085	98	42	1.87	167	2.53
Practical example 8	0.103	97	59	1.88	183	2.48
Comparative example 5	0.122		> 1000	2.68	162	2.59
Practical example 9-a	0.120	90	256	1.75	189	2.47
Practical example 9-b	0.116	92	350	1.82	188	2.47
Practical example 9-c	0.112	92	625	1.93	185	2.50
Practical example 9-d	0.112	93	280	2.08	185	2.50
Practical example 10-a	0.124	89	430	1.88	189	2.46
Comparative example 6	Could not be deposited					

Table 2. Table of Deposition conditions

Conditions	a	b	c	d
Parts by weight of polyphenylene ether solution	70	40	30	20
Parts by weight of methanol	130	160	170	180
Weight ratio of methanol/ toluene	2.5	5.0	7.0	120

Reference example

Dissolution rate of polyphenylene ether obtained in practical example 1, practical example 2, practical example 3, practical example 4, practical example 7, comparative example 3 and comparative example 5 in methyl ethyl ketone was observed. Experiment method has been given below. First, 100 g of methyl ethyl ketone was taken in a round bottom flask and it was slowly stirred at 20°C by using magnetic stirrer. 20 g of polyphenylene ether of each example was added to it. Mixtures excluding polyphenylene ether of comparative example 5 were turbid at first but became clear. Time from adding till the mixture becomes clear was measured (dissolution time). Moreover, state of internal part of flask at the time of dissolution was observed. The results have been presented in table 3 given below.

Table 3. Dissolution test in methyl ethyl ketone

Examples	Dissolution time [min]	Observation
Practical example 1	1.1	
Practical example 2	0.87	
Practical example 3	0.75	
Practical example 4	0.92	

Practical example 7	0.95	
Comparative example 3		Did not dissolved
Practical example 5	30	Lump formed

The dissolution rate at the time of using polyphenylene ether of practical examples was approximately 1 minute and adhesion on the internal walls of flask was not observed. Dissolution rate in case of comparative example 5 was 30 minutes and polyphenylene ether of comparative example 5 solidified and adhered on the internal walls of flask and it did not dissolve.

The present invention has been explained in details with the help of state of practicalization mentioned above, however, it can be changed or modified within the scope of the present invention.

This application is as per Japanese Patent Application (Application 2002 – 63626) dated 8th March 2002 and its contents have been referred to here.

<Industrial applicability>

Low molecular weight polyphenylene ether having specific molecular weight distribution of the present invention possesses high heat resistance and electrical properties and it also has solubility in solvents in powder form and reactivity due to which it is suitable in electronic material application and as improving agent of other resins. Moreover, this low molecular weight polyphenylene ether can be manufactured by the method of the present invention.

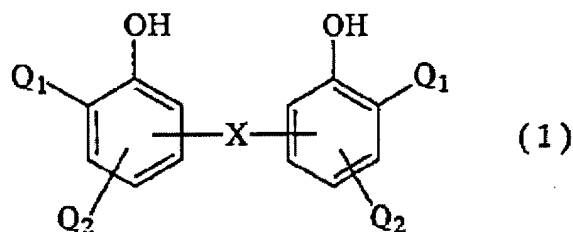
Scope of patent claims

1. The low molecular weight polyphenylene ether has the characteristic of having reduced viscosity measured at 30⁰C over chloroform solution having concentration of 0.5 g/dl, of 0.04 ~ 0.18 dl/g and molecular weight distribution of 1.5 ~ 2.5.
2. The low molecular weight polyphenylene ether described above in (1) in which glass transition temperature (T_g) is shown by the following formula.

$$T_g (^{\circ}\text{C}) > 600 \times [\eta_{sp} / c] + 105$$
3. The polyphenylene ether powder that is formed from low molecular weight polyphenylene ether described above in claim number 1 or 2.
4. The polyphenylene ether powder described above in claim number 3 that has average particle diameter of 5.0 ~ 1000 μm.
5. The polyphenylene ether powder described above in claim number 3 that has average particle diameter of 5.0 ~ 500 μm.
6. The polyphenylene ether powder described above in claim number 3 that has average particle diameter of 5.0 ~ 300 μm.
7. The polyphenylene ether powder described above in claim number 3 that has

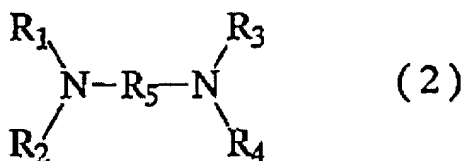
average particle diameter of 5.0 ~ 100 μm .

8. The polyphenylene ether powder described above in claim number 3 that essentially does not contain particles of more than 1000 μm .
9. The low molecular weight polyphenylene ether described above in claim number 1 that is obtained by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas.
10. The low molecular weight polyphenylene ether described above in claim number 9 in which phenol compound is 2, 6 – di methyl phenol.
11. The low molecular weight polyphenylene ether described above in claim number 9 in which phenol compound is mixture of 2, 6 – di methyl phenol and 2, 3, 6 – tri methyl phenol.
12. The low molecular weight polyphenylene ether described above in claim number 9 in which phenol compound is mixture of 2, 6 – di methyl phenol and 2, 6 – di phenyl phenol.
13. The low molecular weight polyphenylene ether described above in claim numbers from 10 ~ 12 in which phenol compound contains divalent phenol shown by the formula (1).



(Wherein, Q1 and Q2 show substitution radical that is hydrogen, alkyl radical, substituted alkyl radical, alalkyl radical, substituted alalkyl radical, aryl radical, substituted aryl radical, alkoxy radical, substituted alkoxy radical or halogen, which can be identical or different: X shows aliphatic hydrocarbon residual radical and their substituted derivatives, oxygen, sulfur or sulfonyl radical and bond position of Q2 and X is ortho or para with respect to phenol hydroxyl radical.)

14. The low molecular weight polyphenylene ether described above in claim number 9 in which catalyst is formed from copper compound, halogen compound and di amine compound shown by the formula (2).



(Wherein, R1, R2, R3 and R4 independently show hydrogen or straight chain or branched alkyl radical having 1 ~ 6 carbon atoms and all these cannot be hydrogen at the same time. R5 shows alkylene radical having 2 ~ 5 carbon atoms having straight chain or methyl branch)

15. The low molecular weight polyphenylene ether described above in claim number 14 in which the catalyst further contains at least tertiary mono amine compound and secondary mono amine compound.
16. The method for manufacture of low molecular weight polyphenylene ether described above in claim number 1 has the following characteristics. Namely, in the method to manufacture low molecular weight polyphenylene ether by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas using good solvent of low molecular weight polyphenylene ether and depositing low molecular weight polyphenylene ether by adding poor solvent to the polyphenylene ether solution obtained by polymerization, the deposition mentioned above is carried out at $-80^{\circ}\text{C} \sim 20^{\circ}\text{C}$.
17. The method described above in claim number 16 in which the poor solvent is alcohol having 1 ~ 10 carbon atoms.
18. The method described above in claim number 16 in which the poor solvent is chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol.
19. The method described above in claim number 18 in which the poor solvent further contains water.
20. The method for manufacture of low molecular weight polyphenylene ether described above in claim number 1 has the following characteristics. Namely, in the method to manufacture low molecular weight polyphenylene ether by polymerizing phenol compound in the presence of catalyst and oxygen-containing gas using good solvent of low molecular weight polyphenylene ether and depositing low molecular weight polyphenylene ether by adding poor solvent to the polyphenylene ether solution obtained by polymerization, polymerization solvent is mixed solvent of 2 or more alcohols.

21. The method described above in claim number 20 in which the mixed solvent is the mixed solvent of 2 or more alcohols having 1 ~ 10 carbon atoms.
22. The method described above in claim number 16 in which the polymerization solvent is mixed solvent of 2 or more alcohols chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol.
23. The method described above in claim number 16 or 20 that includes the process of refining the deposited slurry containing low molecular weight polyphenylene ether by washing and the washing solvent is chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol and ethylene glycol.
24. The method described above in claim number 23 in which the washing solvent further contains water.
25. The method described above in claim number 23 in which the solvent is removed by drying or directly degassing the low molecular weight polyphenylene ether after washing.
26. The method described above in claim number 16 or 20 in which wet low molecular weight polyphenylene ether is obtained by separating it from the deposited slurry containing low molecular weight polyphenylene ether and the solvent is removed by drying or directly degassing it.